# Thermally stable lead(II) amidinates and guanidinates†‡

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The reactions of lithium amidinates and guanidinates [Li(Fiso)] (Fiso = *N*,*N*′-bis(2,6-diisopropylphenyl)formamidinate), [Li(Piso)] (Piso = *N*,*N*′-bis(2,6-diisopropylphenyl)-(*tert*-butyl)amidinate), [Li(CyG)] (CyG = *N*,*N*″-bis(2,6-diisopropylphenyl)-*N*′,*N*′-dicyclohexylguanidinate) and [Li(HDG)] (HDG = *N*,*N*″-bis(2,6-diisopropylphenyl)-*N*′-(2,6-diisopropylphenyl)guanidinate) with anhydrous $PbCl_2$ in THF afforded the amidinate complexes $[Pb(Fiso)_2]$ **1**, and $[Pb(Piso)Cl]_2$ **2**, and the guanidinate complexes $[Pb(CyG)Cl]_2$ **3**, and $[Pb(HDG)Cl]_2$ **4** in moderate yields. The complexes are thermally stable, **2**, **3** and **4** decompose between 163–202 °C whilst **1** melts with decomposition to lead metal at 310 °C. **2**, **3** and **4** are unsymmetrical dimers in the solid state but their NMR data suggested fluxional behaviour in solution. Storing the yellow crystals of $[Pb(CyG)Cl]_2$ **3** for one week in the perfluorinated crystallography oil under air resulted in oxygen incorporation into one isopropyl group of the CyG ligand giving a mixed amidinate-alkoxide dianion (CyGO) and afforded some new colourless crystals of $[(CyGO)Pb]_2$ **5** that were characterised by a X-ray single crystal structure determination.

## Introduction

Metal organoamides (*i.e.* compounds with a $M–NR_2$ moiety) are a significant and well populated compound class that have been established for many years. Indeed, Lappert's seminal book *Metal and Metalloid Amides*, published in 1980, listed 100s of examples from across the periodic table. However, only three complexes were given for lead(II), and one of these was described as unstable.[1] In the subsequent 25 years little has changed and lead(II) organoamides remain underdeveloped.[2] This is undoubtedly due to the diminishing industrial utilization of lead compounds amid significant environmental and health concerns[3] as well as the inherent low stability of these complexes with respect to precipitation of lead(0). Stabilization of unusual metal–organic species has been a major research focus and a common strategy to achieve this goal has been the use of very bulky ligand systems. Monoanionic, bidentate organoamido frameworks with large groups such as 2,6-diisopropylphenyl attached to the donor nitrogen atoms have proven extremely useful in this context. Relevant examples include the diketiminate[4] and amidinate[5,6] classes (Fig. 1), where the metal, bound to the two nitrogen atoms, is enveloped by the peripheral aryl groups leaving a restricted reactivity opening. Further, the effective size of the ligand can be increased by substitution of the backbone which pushes the aryl groups closer to the metal binding sites. A popular example is the 'nacnac' ligand which has found applications in catalysis, bioinorganic molecules, organic-inorganic hybrids, multiply bonded M–X (X = C, N, P) species and low coordinate, low valent complexes.[4]

We have recently explored the use of very bulky amidinate (and related guanidinate) ligands for development of low coordinate, low oxidation state main group and rare earth species.[6] In this contribution, we report the synthesis of a number of thermally stable and rare lead(II) complexes using these bulky ligand systems and compare their synthetic and structural outcomes. These studies complement recent reports of the three coordinate lead(II) nacnac complexes [Pb(nacnac)X] (X = Cl, Br, I).[2a]

## Experimental

The lead complexes described herein are air and water sensitive, hence all operations were carried out in an inert atmosphere (purified $N_2$ or Ar) involving conventional glove-box and Schlenk techniques. Solvents were purified, dried and deoxygenated by refluxing over and distillation from sodium-benzophenone, whilst $C_6D_6$ was dried over Na followed by vacuum transfer to greaseless Schlenk tubes and stored under purified argon or nitrogen. $^1H$ and $^{13}C$ NMR spectra

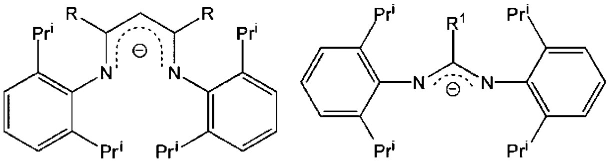

**Fig. 1** Very bulky bidentate organoamido frameworks include diketiminate ligands (such as nacnac, R = $CH_3$) or amidinate ligands (in this study Fiso, $R^1$ = H; Piso, R = *t*-Bu; CyG, R = $NCy_2$; HDG, R = $NH(C_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)$.

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were recorded on a Bruker AM 300 or DRX 400 spectrometer; chemical shifts are referenced to internal solvent resonances and reported relative to $SiMe_4$. IR data (4000–650 $cm^{-1}$) were obtained for Nujol mulls sandwiched between NaCl plates with Perkin-Elmer 1600 FTIR. EI mass spectra and accurate mass EI spectra were obtained from the EPSRC National Mass Spectrometric Service at Swansea University. Lead(II) chloride was obtained from Aldrich and sublimed before use. The formamidines FisoH,[7a] PisoH,[6g,7b] and the guanidines CyGH,[6d] HDGH[7c] were synthesised by the reported methods.

### $[Pb(Fiso)_2]$ 1

*n*-BuLi (2.90 mL of a 1.6 M solution in hexanes, 4.78 mmol) was added at 0 °C to a solution of [(Fiso)H] (1.65 g, 4.53 mmol) in THF (40 mL) and stirred for 1 h at room temperature. The solution was cooled to −80 °C and $PbCl_2$ (1.85 g, 6.65 mmol) was added. The reaction mixture was slowly warmed to room temperature and stirred overnight. The mixture was filtered and concentrated under reduced pressure to *ca.* 15 mL. Cooling to −30 °C gave yellow crystals of $[Pb(Fiso)_2]$ **1**. Concentration of the supernatant solution and cooling led to a further crop of **1**. Yield: 0.85 g (40%). Mp: 310 C (melts with decomp. to $Pb^0$). $^1H$ NMR (300 MHz, $C_6D_6$, 296 K): 1.12 (d, $J$ = 6.7 Hz, 24H, $CH(CH_3)_2$), 1.17 (d, $J$ = 6.7 Hz, 24H, $CH(CH_3)_2$), 3.45 (sept, $J$ = 6.7 Hz, 8H, $CH(CH_3)_2$), 6.94–7.27 (m, 12H, ArH), 10.81 (s, 2H, $N_2CH$). $^{13}C$ NMR (75.5 MHz, $C_6D_6$, 296 K): 24.2 ($CH(CH_3)_2$), 25.1 ($CH(CH_3)_2$), 28.7 ($CH(CH_3)_2$), 29.0 ($CH(CH_3)_2$), 123.7 (ArC), 123.8 (ArC), 125.5 (ArC), 144.2 (ArC), 163.5 ($N_2CH$). IR ($\nu$/$cm^{-1}$ Nujol): 1666 (s), 1592 (m), 1378 (m), 1319 (s), 1270 (s), 1183 (s), 1098 (s), 986 (m), 946 (m), 799 (m), 754 (s). MS (EI): $m/z$ (%) = 891 (3, $M^+ - C_3H_7$), 571 (100, FisoPb + $H^+$), 529 (17, FisoPb − $C_3H_6{}^+$), 363 (41, $FisoH^+$).

### $[Pb(Piso)Cl]_2$ 2

*n*-BuLi (2.00 mL of a 1.6 M solution in hexanes, 3.20 mmol) was added to a solution of [(Piso)H] (1.33 g, 3.16 mmol) in THF (40 mL) and stirred for 1 h at room temperature. The solution was cooled to −80 °C and $PbCl_2$ (1.00 g, 3.60 mmol) was added. The reaction mixture was slowly warmed to room temperature and stirred overnight. The solvent was removed under reduced pressure and the residue was extracted into hexane (50 mL). Concentration of the solution under reduced pressure to *ca.* 15 mL and cooling to −30 °C gave yellow crystals of [Pb(Piso)Cl] **2**. Yield: 0.48 g (23%). Mp: 198–202 °C (decomp.). $^1H$ NMR (400 MHz, $C_6D_6$, 296 K): 1.06 (s, 18H, $C(CH_3)_3$), 1.35 (d, $J$ = 6.7 Hz, 24H, $CH(CH_3)_2$), 1.42 (d, $J$ = 6.7 Hz, 24H, $CH(CH_3)_2$), 3.96 (sept, $J$ = 6.7 Hz, 8H, $CH(CH_3)_2$), 7.00–7.33 (m, 12H, ArH). $^{13}C$ NMR (100.3 MHz, $C_6D_6$, 296 K): 23.1 ($C(CH_3)_3$), 28.9 ($CH(CH_3)_2$), 29.1 ($CH(CH_3)_2$), 29.8 ($CH(CH_3)_2$), 53.0 ($C(CH_3)_3$), 123.7 (ArC), 126.3 (ArC), 141.1 (ArC), 144.8 (ArC), 176.2 ($N_2C$). IR ($\nu$/$cm^{-1}$ Nujol): 1614 (s), 1586 (m), 1377 (s), 1326 (m), 1255 (m), 1168 (m), 1100 (m), 1017 (m), 800 (m), 758 (m). MS (EI): $m/z$ (%) = 662 (3, $\frac{1}{2}M^+$), 627 (2, $\frac{1}{2}M^+ - Cl$), 619 (5, $\frac{1}{2}M^+ - C_3H_7$), 420 (18, $PisoH^+$). Accurate mass for $C_{29}H_{43}N_2Pb_1Cl_1$; Calcd: 662.2876; Found: 662.2875.

### $[Pb(CyG)Cl]_2$ 3

*n*-BuLi (0.66 mL of a 1.6 M solution in hexanes, 1.06 mmol) was added to a solution of [(CyG)H] (0.54 g, 1.00 mmol) in THF (20 mL) and stirred for 1 h at room temperature. The solution was cooled to −80 °C and $PbCl_2$ (0.32 g, 1.15 mmol) was added. The reaction mixture was slowly warmed to room temperature and stirred overnight. The solvent was removed under reduced pressure and the residue was extracted into hexane (40 mL). Concentration of the solution under reduced pressure to *ca.* 12 mL and cooling to −30 °C gave yellow crystals of $[Pb(CyG)Cl]_2$ **3**. Yield: 0.23 g (29%). Mp: 200–203 °C (decomp.). $^1H$ NMR (300 MHz, $C_6D_6$, 296 K): 0.73–0.94 (m, 16H, $CH_2$), 1.34 (d, $J$ = 6.8 Hz, 24H, $CH(CH_3)_2$), 1.42 (d, $J$ = 6.8 Hz, 24H, $CH(CH_3)_2$), 1.36–1.90 (m, 24H, $CH_2$), 3.47 (m, 4H, CHN), 3.91 (sept, $J$ = 6.7 Hz, 8H, $CH(CH_3)_2$), 6.92–7.31 (m, 12H, ArH). $^{13}C$ NMR (75.5 MHz, $C_6D_6$, 296 K): 23.3 (CyC), 26.1 (CyC), 27.5 ($CH(CH_3)_2$), 28.4 ($CH(CH_3)_2$), 30.4 ($CH(CH_3)_2$), 35.5 (CyC), 59.1 (HCN), 123.9 (ArC), 125.8 (ArC), 140.5 (ArC), 145.3 (ArC), 167.7 ($N_3C$). IR ($\nu$/$cm^{-1}$ Nujol): 1611 (m), 1583 (m), 1321 (m), 1278 (m), 1241 (m), 1164 (m), 1109 (m), 1022 (m), 796 (m), 752 (m). MS (EI): $m/z$ (%) = 750 (3, $\frac{1}{2}M^+ - Cl$), 543 (22, $CyGH^+$). Storing the yellow crystals of $[Pb(CyG)Cl]_2$ **3** for one week in the perfluorinated crystallography oil in air afforded some new colourless crystals of $[(CyGO)Pb]_2$ **5** that were (only) characterised by a X-ray single crystal determination.

### $[Pb(HDG)Cl]_2$ 4

*n*-BuLi (0.62 mL of a 1.6 M solution in hexanes, 0.99 mmol) was added to a solution of [(HDG)H] (0.51 g, 0.94 mmol) in THF (20 mL) and stirred 1 h at room temperature. The solution was cooled to −80 °C and $PbCl_2$ (0.35 g, 1.26 mmol) was added. The reaction mixture was slowly allowed to warm to room temperature and stirred overnight. The mixture was filtered, the solvent was removed under reduced pressure and the residue was extracted into toluene (20 mL). Concentration of the solution under reduced pressure to *ca.* 6 mL and cooling to −30 °C gave yellow crystals of [Pb(HDG)Cl] **4**. Yield: 0.22 g (30%). Mp: 163 °C (decomp.). $^1H$ NMR (300 MHz, $C_6D_6$, 296 K): 0.88 (br d, $J$ = 6.8 Hz, 24H, $CH(CH_3)_2$), 1.18 (d, $J$ = 6.8 Hz, 24H, $CH(CH_3)_2$), 1.25 (br d, $J$ = 6.8 Hz, 24H, $CH(CH_3)_2$), 3.19 (sept, $J$ = 6.7 Hz, 4H, $CH(CH_3)_2$), 3.83 (m, broad, 8H, $CH(CH_3)_2$), 5.24 (s, 2H, NH), 6.87–7.21 (m, 18H, ArH). $^{13}C$ NMR (75.5 MHz, $C_6D_6$, 296 K): 22.1 ($CH(CH_3)_2$), 24.1 (br, $CH(CH_3)_2$), 28.7 ($CH(CH_3)_2$), 28.8 ($CH(CH_3)_2$), 29.6 ($CH(CH_3)_2$), 123.4 (ArC), 123.7 (ArC), 126.5 (ArC), 128.9 (ArC), 129.7 (ArC), 133.4 (ArC), 146.7 (ArC), 148.6 (ArC), 164.4 ($N_3C$). MS (EI): $m/z$ (%) = 781 (1, $\frac{1}{2}M^+$), 539 (28, $HDGH^+$), 496 (62, $HDGH^+ - C_3H_7$).

### Structure determinations

Single crystals suitable for X-ray diffraction were grown from hexane (**1**, **2**) or toluene (**3**, **4**). Full spheres or hemispheres ($2\theta_{max}$ 50–55°) of CCD area-detector diffractometer data were measured (Enraf Nonius KAPPA CCD, 1.0° frames, $\varphi$- and $\omega$-scans, monochromatic Mo-K$\alpha$ radiation, $\lambda$ = 0.71073 Å; $T$ *ca.* 123 K) yielding $N_t$ reflections, these merging to $N$ independent data ($R_{int}$ quoted) after empirical/multi-scan absorption correction (SORTAV).[8a] Full matrix least squares refinement on $F^2$ (SHELX97)[8b] with anisotropic displacement parameter forms for non-hydrogen atoms (unless otherwise noted) and hydrogen atoms placed in calculated positions, constrained to ride on the parent atoms, yielded final residuals $R$ ($I > 2\sigma(I)$) and w$R_2$ (all data).

### Crystal/refinement data

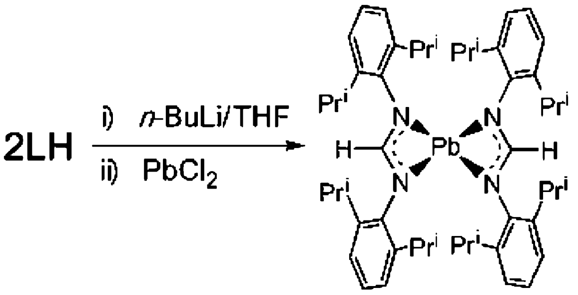
**1.** [Pb(Fiso)$_2$], $C_{50}H_{70}N_4Pb$, $M$ = 934.29, monoclinic, $P2_1/c$, $a$ = 14.9163(3), $b$ = 16.1789(3), $c$ = 20.8178(5) Å, $\beta$ = 110.090(1)°, $V$ = 4718.26(17) Å$^3$. $Z$ = 4. $D_c$ = 1.315 g cm$^{-3}$. $\mu_{Mo}$ = 3.611 mm$^{-1}$; specimen: 0.25 × 0.20 × 0.10 mm; $T'_{min,max}$ = 0.41, 0.69, $N_t$ = 25834, $N$ = 8289 ($R_{int}$ = 0.072), $R$ = 0.058, w$R_2$ = 0.146. Carbon atoms C(12) and C(13) were modelled as disordered over two positions (0.75 : 0.25 after trial refinement) and were refined with restrained geometry and anisotropic thermal parameters. Large ADP for carbon atoms C(24) and C(25) suggested similarly disordered *i*-Pr groups but this could not be adequately modelled with the current data. The largest residual electron density maximum (3.34 e Å$^3$) was located *ca.* 0.5 Å from Pb(1).

**2.** [Pb(Piso)Cl]$_2$, $C_{58}H_{86}Cl_2Pb_2$, $M$ = 1324.59, triclinic, $P\bar{1}$, $a$ = 10.0568(3), $b$ = 11.0744(2), $c$ = 14.5525(4) Å, $\alpha$ = 69.707(2), $\beta$ = 73.897(1), $\gamma$ = 74.244(1)°, $V$ = 1432.60(7) Å$^3$, $Z$ = 1 (dimer). $D_c$ = 1.535 g cm$^{-3}$. $\mu_{Mo}$ = 6.00 mm$^{-1}$; specimen: 0.25 × 0.20 × 0.12 mm; $T'_{min,max}$ = 0.35, 0.54, $N_t$ = 18845, $N$ = 5560 ($R_{int}$ = 0.070), $R$ = 0.037, w$R_2$ = 0.080.

**3·3PhMe.** [Pb(CyG)Cl]$_2$·3PhMe, $C_{95}H_{136}Cl_2Pb_2$, $M$ = 1847.38, triclinic, $P\bar{1}$, $a$ = 13.2064(3), $b$ = 13.3847(3), $c$ = 13.9337(4) Å, $\alpha$ = 63.026(1), $b$ = 80.217(1), $g$ = 79.878(1)°, $V$ = 2149.88(9) Å$^3$, $Z$ = 1. $D_c$ = 1.427 g cm$^{-3}$. $\mu_{Mo}$ = 4.021 mm$^{-1}$; specimen: 0.25 × 0.25 × 0.20 mm; $T'_{min,max}$ = 0.43, 0.50, $N_t$ = 19 429, $N$ = 9765 ($R_{int}$ = 0.054), $R$ = 0.041, w$R_2$ = 0.099. The lattice PhMe molecules were modelled as disordered over two positions, C(41)–C(47) (occupancies 0.54 : 0.46), the second component of C(48)–C(54) related by inversion, and were refined with isotropic thermal parameters and restrained geometry. The largest residual electron density maximum (2.21 e Å$^3$) was located *ca.* 0.9 Å from Pb(1).

**4·2PhMe.** [Pb(HDG)Cl]$_2$·2PhMe, $C_{88}H_{120}Cl_2N_6Pb_2$, $M$ = 1747.20, triclinic, $P\bar{1}$, $a$ = 10.9449(4), $b$ = 13.1345(4), $c$ = 15.3776(7) Å, $\alpha$ = 109.593(2), $\beta$ = 98.675(2), $\gamma$ = 95.682(3)°, $V$ = 2032.07(14) Å$^3$, $Z$ = 2. $D_c$ = 1.428 g cm$^{-3}$. $\mu_{Mo}$ = 4.250 mm$^{-1}$; specimen: 0.20 × 0.15 × 0.10 mm; $T'_{min,max}$ = 0.43, 0.63, $N_t$ = 21071, $N$ = 7131 ($R_{int}$ = 0.104), $R$ = 0.056, w$R_2$ = 0.087.

**5·3PhMe.** [Pb(CyGO)]$_2$·3PhMe, $C_{95}H_{134}N_6O_2Pb_2$, $M$ = 1806.46, monoclinic, $P2_1/c$, $a$ = 10.0458(2), $b$ = 24.5646(6), $c$ = 17.3771(4) Å, $\beta$ = 97.058(1)°, $V$ = 4255.67(17) Å$^3$, $Z$ = 4. $D_c$ = 1.410 g cm$^{-3}$. $\mu_{Mo}$ = 4.002 mm$^{-1}$; specimen: 0.20 × 0.15 × 0.08 mm; $T'_{min,max}$ = 0.48, 0.72, $N_t$ = 35104, $N$ = 8328 ($R_{int}$ = 0.086), $R$ = 0.055, w$R_2$ = 0.083. The lattice PhMe molecules were modelled as disordered over two positions, C(38)–C(44) (occupancies 0.51 : 0.49), the second component of C(45)–C(51) related by inversion, and were refined with restrained geometry and anisotropic thermal parameters.



**Scheme 1** Synthesis of [Pb(Fiso)$_2$] (**1**) (L = Fiso).

## Results and discussion

The lithium salt of the bulky formamidinate ligand Fiso (= $N,N'$-bis(2,6-diisopropylphenyl)formamidinate)[9] prepared by *in situ* reaction of the parent amine, reacted readily with $PbCl_2$ in THF/hexane mixtures to afford crystalline, yellow, hexane soluble [Pb(Fiso)$_2$] (**1**) (Scheme 1). NMR characterisation of **1** showed four distinct $^{13}$C resonances for the *i*-Pr methyl groups (but only two equal intensity doublets were resolved in the $^1$H NMR spectrum) but only a single formamidinate NC(H)N backbone resonance. This is consistent with observations for [Pb(nacnac)Cl][2a] and similarly suggests that **1** has a pyramidal lead environment. Indeed, the crystal structure of **1** (Fig. 2) shows a monomeric four coordinate complex with the lead atom bound to two bidentate Fiso ligands with the amidinate (NCN) coordination planes approximately *cisoid* (dihedral angle of 76.2(2)°). Each Fiso ligand displays asymmetric Pb–N distances with one *ca.* 0.1 Å longer than the other. Comparably dissimilar Pb–N distances (2.311(3)–2.669(3) Å) are observed in the bis(β-diketiminate)lead(II) complex [Pb(L)$_2$] (L = {N(SiMe$_3$)C(Ph)}$_2$CH),[2b] contrasting the near symmetrical binding for the less crowded (β-diketiminate)-chlorolead(II) complex [Pb(nacnac)Cl] (2.280(2), 2.290(2) Å).[2a] The *cisoid* coordination of the two Fiso ligands leaves exposed a significant area of the lead coordination sphere. This space is largely occupied by the pendant *i*-Pr groups which have the methine C–H directed toward the metal centre with Pb···H distances 2.65–2.95 Å suggestive of agostic interactions. Even so, there remains an unoccupied 'hole' in the molecule (Fig. 2(b)) plausibly indicating a stereochemically active lone pair on lead. In a study on the role of the lone pair in lead stereochemistry, a similar "hemidirected" coordination environment was typical for low coordination number (2–5) lead(II) with hard donor ligands.[10] However, DFT calculations on [M(nacnac)X] complexes (M = Ge, Sn, Pb) have suggested that the lone pair on lead is more diffuse than for the lighter group 14 congeners.[2a] In the current structure, close approach of a neighbouring molecule is prevented by the protruding Me groups of the Fiso ligands (shortest intermolecular distance to Pb(1) 4.18 Å).

Analogous reactions of the lithium salts of the more bulky amidinate Piso = $N,N'$-bis(2,6-diisopropylphenyl)-*tert*-butylamidinate) and related guanidinate (CyG = $N,N''$-bis(2,6-diisopropylphenyl)-$N',N'$-dicyclohexylguanidinate, HDG = (HDG = $N,N''$-bis(2,6-diisopropylphenyl)-$N'$-2,6-diisopropylphenylguanidinate) ligands with $PbCl_2$, followed by removal of the THF and extraction into hexane, yielded the chloride

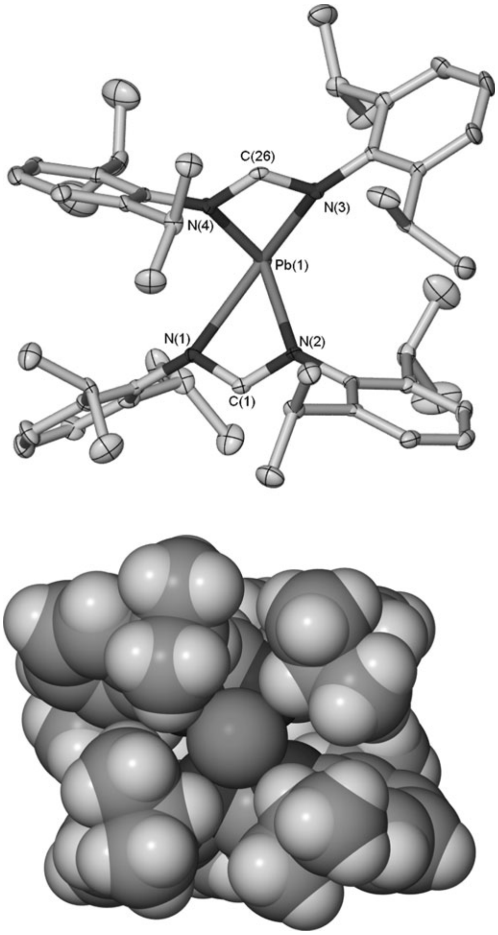
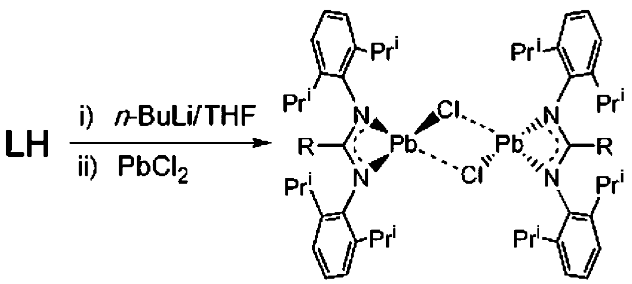


**Fig. 2** Molecular diagram of [Pb(Fiso)$_2$] (**1**): (a) with 30% thermal ellipsoids and hydrogen atoms omitted for clarity; (b) reverse angle view with atoms as space filling representations showing the vacancy in the lead coordination sphere. Selected bond distances: Pb(1)–N(1) 2.465(7), Pb(1)–N(2) 2.332(6), Pb(1)–N(3) 2.463(6), Pb(1)–N(4) 2.359(6) Å.

complexes [Pb(L)Cl]$_2$ (L = Piso **2**, CyG **3**, HDG **4**) in moderate yields (Scheme 2). There was no spectroscopic evidence of other species in solution, and whilst the residual material after hexane extraction was coloured (suggesting retention of a lead species), the material was not soluble in common solvents (*e.g.* THF) and thus unlikely to be a putative PbL$_2$ complex. The products were highly soluble in hexane (plausibly accounting for the moderate isolated yields) and appeared stable in solution for several weeks with respect to precipitation of lead(0). These synthetic results were satisfyingly predictable on the basis of the relative sizes of the respective ligands. Thus, whilst the smaller Fiso gave the Pb(L)$_2$ derivative (see above), the larger Piso, CyG and HDG gave only the Pb(L)Cl, despite variation of the ratio of the reagents. These are in agreement with our findings for germanium(II)[6g] and aluminium(III)[6i] and demonstrate the tuneable nature of the amidinate ligand framework and that these effects can be transferred to divergent (and larger) metal systems.



**Scheme 2** Synthesis of [Pb(L)Cl]$_2$ complexes (L = Piso, R = *t*-Bu; CyG, R = NCy$_2$; HDG, R = N(H)C$_6$H$_3$-2,6-*i*-Pr$_2$.

Mass spectra of the three [Pb(L)Cl]$_2$ complexes (L = Piso **2**, CyG **3**, HDG **4**) showed Pb(L)Cl$^+$ ions as the highest observed mass species suggesting monomeric structures as found for [Pb(nacnac)X] (X = Cl, Br, I). However, the crystal structures of all three complexes (Fig. 3–5) showed each to be a loosely associated chloride bridged dimer. In **2–4** the lead centres are bound to a single bidentate amidinate or guanidinate ligand and one chloride ligand having normal terminal Pb–Cl distances. For example, the value for three coordinate [Pb(nacnac)Cl] is 2.5653(7) Å,[2a] whilst those for four coordinate [Pb(L)(μ-Cl)]$_2$ (L = C(SiMe$_3$)$_2$(SiMe$_2$OMe)) are 2.680(5) and 2.868(5) Å.[11] The Pb–N distances for **2** and **3** are virtually identical, indicating symmetrical binding of the amidinate or guanidinate ligand. For **4** there is a slight degree asymmetry with a difference of *ca.* 0.06 Å between the two Pb–N distances. Additional to the primary amidinate/guanidinate and chloride ligation, in each complex there is a longer Pb···Cl contact to the Cl ligand of a neighbouring molecule (related by inversion symmetry) with bond distances (Å) 3.037(2) **4**–3.260(2) **2**. The shorter two contacts are comparable to those observed in polymeric lead(II) chloride complexes, *e.g.* [PbCl$_2$(L)]$_n$ (L = phen, bpy; Pb–Cl 2.858(3), 3.023(3) Å, in which far infrared data suggested only weak Pb–Cl binding.[12] For **2** and **3**, the N–Pb(1)–Cl(1) angles are all approximately equal as was observed for monomeric [Pb(nacnac)Cl] (although the current values are larger due to the smaller bite angle of the amidinate NCN backbone), suggesting that the molecular association is sufficiently weak as to not perturb the lead coordination environment. However, for **4**, which has a Pb···Cl distance only marginally shorter than for **3**, there is one acute and one obtuse N–Pb(1)–Cl(1) angle, which, along

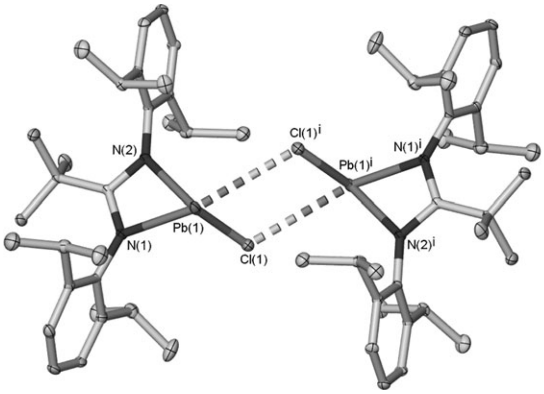


**Fig. 3** Molecular diagram of [Pb(Piso)Cl]$_2$ shown with 30% thermal ellipsoids and hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (°): Pb(1)–N(1) 2.330(4), Pb(1)–N(2) 2.326(4), Pb(1)–Cl(1) 2.571(2), Pb(1)–Cl(1$^i$) 3.260(2); Cl(1)–Pb(1)–Cl(1$^i$) 78.49(5), N(1)–Pb(1)–Cl(1) 93.6(1), N(1)–Pb(1)–Cl(1$^i$) 160.1(1), N(2)–Pb(1)–Cl(1) 98.2(1), N(2)–Pb(1)–Cl(1$^i$) 106.1(1). Symmetry operator: $^i$$-x$, $-y$, $-z$.

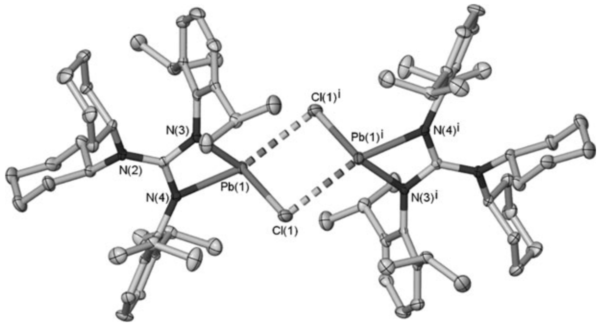


**Fig. 4** Molecular diagram of $[\mathrm{Pb(CyG)Cl}]_2$ shown with 50% thermal ellipsoids and hydrogen atoms and lattice toluene omitted for clarity. Selected bond distances (Å) and angles (°): Pb(1)–N(3) 2.311(4), Pb(1)–N(4) 2.360(3), Pb(1)–Cl(1) 2.598(1), Pb(1)–Cl(1$^{i}$) 3.093(1); Cl(1)–Pb(1)–Cl(1$^{i}$) 78.43(3), Cl(1)–Pb(1)–N(3) 101.99(9), Cl(1)–Pb(1)–N(4) 96.10(8), N(3)–Pb(1)–Cl(1$^{i}$) 93.64(8), Symmetry operator: $^{i}2 - x, 2 - y, 1 - z$.

with the asymmetric ligand binding, clearly indicates a distortion of the coordination environment caused by the dimerisation. The structures of **2** and **3** can be compared with those of their tin(II) analogues, [Sn(Piso)Cl][13] and [Sn(CyG)Cl],[6h] which show very similar pyramidal three coordinate metal environments, but are isolated monomers in the crystal lattice and do not form the loose association observed in the current lead(II) structures. With the bridging chloride interactions included, the lead coordination environments in complexes **2–4** are distinctly pyramidal.

A small sample of yellow crystals of [Pb(CyG)Cl], covered in a viscous fluorocarbon oil (used to mount crystals for X-ray analysis) was exposed to air. Surprisingly, new colourless crystals formed which were analysed by X-ray structure determination. The product, $[\mathrm{Pb(CyGO)}]_2$ (**5**) (Fig. 5) was shown to contain a modified CyG ligand in which one of the substituent *i*-Pr groups on the aryl rings had converted to an alkoxide moiety. The structure is dimeric, bridged by the alkoxide oxygen atoms and both lead atoms each bound to the amidinate fragment by both nitrogen atoms. The Pb–N distances are asymmetric with that to N(1) *ca.* 0.3 Å longer than for N(2). The latter is attached to the alkoxide substituted aryl group which is also bound to Pb(1) and this may cause the distortion of the amidinate binding. The Pb(1)–N(2) distance is shorter than those observed in **1–4** above. Four coordinate lead(II) complexes with bridging alkoxide ligands have been observed previously, *viz.* $[\mathrm{Pb(OCH(CF_3)_2)(\mu\text{-}OCH(CF_3)_2)(py\text{-}4\text{-}NMe_2)}]_2$ and $[\mathrm{Pb(OCH(CF_3)_2)_2(\mu\text{-}OCH(CF_3)_2)}]_2[\mathrm{Me_2NH_2}]_2$, and have similar Pb–O distances (2.247(6)–2.716(6) Å and 2.243(6)–2.659(5) Å).[14] The origin of **5** is speculative given the uncontrolled nature of its formation. However, recent work by Roesky and co-workers have shown that deliberate oxidation of aluminium nacnac complexes by either *t*-BuOOH or molecular oxygen leads to an analogous modification of the nacnac ligands and the formation of a $\mathrm{ArCMe_2O^-}$ appended to the ketiminate backbone.[15] Thus, it seems likely that **5** results from a reaction of **3** with molecular oxygen, the protective covering of the hydrophobic fluorocarbon oil allowing only slow ingress of oxygen and preventing further hydrolysis and/or total degradation of the complex. Overall, $O_2$ has been added to the molecule whilst two equivalents of HCl have been eliminated and presumably this is a radical process induced by the di-radical $O_2$ species. A deliberate synthesis of **5** was not attempted (Fig. 6).

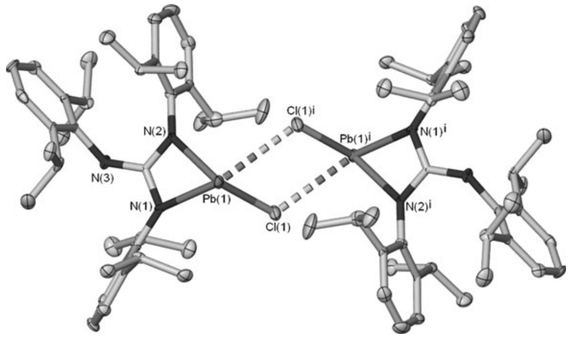


**Fig. 5** Molecular diagram of $[\mathrm{Pb(HDG)Cl}]_2$, shown with 50% thermal ellipsoids and hydrogen atoms and lattice PhMe omitted for clarity. Selected bond distances (Å) and angles (°): Pb(1)–N(1) 2.405(5), Pb(1)–N(2) 2.346(5), Pb(1)–Cl(1) 2.619(2), Pb(1)–Cl(1$^{i}$) 3.037(2); Cl(1)–Pb(1)–Cl(1$^{i}$) 78.14(6), Cl(1)–Pb(1)–N(1) 89.3(1), Cl(1)–Pb(1)–N(2) 106.5(1), N(1)–Pb(1)–Cl(1$^{i}$) 151.2(1), N(2)–Pb(1)–Cl(1$^{i}$) 102.2(1). Symmetry operator: $^{i}1 - x, 1 - y, 1 - z$.

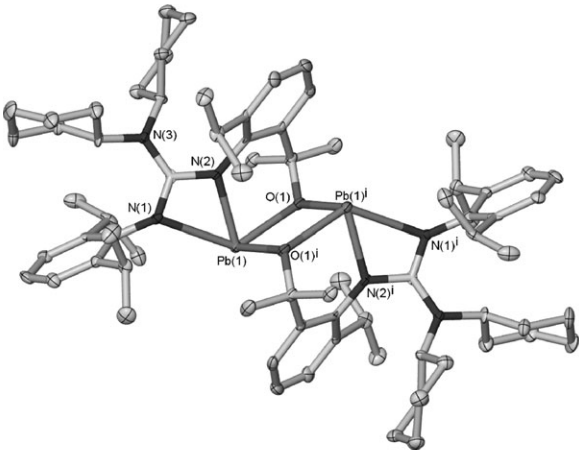


**Fig. 6** Molecular diagram of $[\mathrm{Pb(CyGO)}]_2$ shown with 50% thermal ellipsoids and hydrogen atoms and lattice toluene omitted for clarity. Selected bond distances (Å) and angles (°): Pb(1)–N(1) 2.633(4), Pb(1)–N(2) 2.282(4), Pb(1)–O(1) 2.345(4), Pb(1)–O(1i) 2.278(3); O(1)–Pb(1)–O(1i) 77.8(1), N(1)–Pb(1)–O(1) 129.5(1), N(1)–Pb(1)–O(1i) 106.9(1), N(2)–Pb(1)–O(1) 76.7(1), N(2)–Pb(1)–O(1i) 90.2(1). Symmetry operator: i $-x, 1 - y, 1 - z$.

## Conclusions

The results presented herein show that bulky bis(2,6-diisopropyl)-amidinate and -guanidinate ligands are suitable for the isolation of thermally stable lead(II) organoamide complexes. As we have found for other metal systems, the number of ligands that can fit around a single metal centre is controlled by the steric size of the ligand. Thus, the smaller Fiso allows two ligands per metal (*i.e.* $\mathrm{PbL_2}$) whereas the larger Piso, CyG and HDG allow only one (*i.e.* PbLX). The retention of one reactive halide functionality in the latter class is significant and enables either formation of further derivatives or as a leaving group for reduction reactions aimed at sub-valent species.[16]

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